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Experimental and modelling study of storage of CO_2 and impurities in a depleted gas field in northeast Netherlands

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Abstract

In order to investigate the effects of impurities on subsurface storage of CO_2, experiments were carried out on Permian Rotliegend reservoir and Zechstein caprock core samples at subsurface conditions of 300 bar and 100° C. The experiments were performed in the presence of brine and the following gas compositions: CO_2, CO_2+5000 ppm H_2S, CO_2+100 ppm H_2S and CO_2+100 ppm SO_2 for a 30 day duration. Following CO_2 injection, permeability of the reservoir and caprock samples increased by 10-30% and by a factor of 3-10 respectively. After co-injection of 5000 ppm H_2S permeability of both reservoir and caprock samples reduced significantly. When the concentration of H_2S was reduced to 100 ppm, minimal variation of permeability took place because the dissolution of minerals was balanced with the precipitation of secondary phases. In the case of co-injection of 100 ppm SO_2 permeability of reservoir samples increased by a factor of 1.18 to 2.2. In the caprock samples permeability changed by a factor of 0.8 to 23.

In addition, in order to determine long term (>100 years) interaction between CO_2 and the reservoir mineralogy we need to rely on modelling programs. This requires accurate and fit for purpose input parameters, associated with the lithological composition of reservoirs and seals at the storage site. For this purpose, we specifically focused on the reactive surface area of minerals, which we measured by scanning electron microscopy. Using the range of measured reactive surface area of minerals as an input in the modelling software, we could obtain the distribution of the sequestered CO_2 as a mineral (3-9 kg of CO_2/ m^3).

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Keywords: CO_2 storage, impurities, reactive surface area

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Introduction

Capture, transport and storage of CO_2 (CCTS) in depleted oil and gas fields is generally considered to be a valid option to reduce anthropogenic carbon dioxide (CO_2) emissions. Several physical and chemical trapping mechanisms are active in the reservoir to retain CO_2 and reduce its mobility. Dependent on the source and the capturing technology, a CO_2 product stream will contain impurities such as H_2S, SO_2, NO_x, H_2, Ar, CO and NH_3 [1]. These impurities can have additional effects on the transport and/or storage phases of the CCTS chain. The degree of purification and hence the cost of capture is determined by the tolerance level of impurities in the transport and storage systems. During transport the degree of purity of CO_2 determines the energy requirements and the integrity of the infrastructure. Phase separation, hydrate formation and the presence of corrosive components in CO_2 transport are directly related to the presence of impurities. With respect to subsurface storage, impurities in CO_2 affect well integrity and injectivity, but also long-term cap-rock seal integrity and hence risk of leakage [2].

Since the cost of CO_2 purification is high, the economic viability of the chain would improve if some of these impurities can be left in the flue gas during capture. The question is therefore: what type and quantity of impurities can be left in the injected CO_2 in order to reduce the cost of capture without affecting the integrity of transport and storage systems?

In recent years different modelling studies have been carried out on the effects of impurities in subsurface storage of CO_2. Waldmann et al. [3] used PHREEQC [4] software and modeled CO_2 and SO_2 co-injection in Triassic Buntsandstein. The results revealed an enhanced level of K-feldspar dissolution next to anhydrite precipitation. Koenen et al. [5] utilized the same software and modeled the impact of two CO_2 streams emanated from the pre-combustion and oxy-fuel capturing process, which included the presence of multiple impurities such as SO_2, H_2S, N_2, in a depleted gas field in the Netherlands. They concluded that the short-term effects of impurities are insignificant compared to injection of pure CO_2. In the long-term, the presence of impurities leads to minor differences in mineralogy. Furthermore they concluded that the increase in porosity caused by pure CO_2 could be counteracted by the presence of impurities due to the precipitation of secondary minerals like alunite and nontronite. Xu et al. [6] used TOUGHREACT to model SO_2 and H_2S co-injection with CO_2. They concluded that the co-injection of SO_2 with CO_2 leads to the appearance of a larger and stronger acidified zone around the wellbore due to the formation of strong sulfuric acid. In addition, several researchers have developed new equations of state for modeling of subsurface storage of impure CO_2 [7,8].

In contrast to the considerable number of modeling studies, at least to the best of our knowledge, only few experimental studies have been carried out on effects of impurities on subsurface storage of CO_2. For example, Bachu and Benion [9] investigated the chromatographic partitioning of H_2S, SO_2, CH_4 and N_2. The results revealed that the impurities would chromatographically partition on the front end of the gas plume, advancing through the water-saturated porous medium due to their different solubility. Wilke et al. [1] carried out 42 days mono- mineral batch experiments with pure and impure (0.5% NO_2 or SO_2) CO_2 injection on rock forming minerals (albite, microcline, calcite, dolomite, anhydrite, kaolinite and biotite). Nitric and sulfuric acid formed following NO_2 and SO_2 co-injection respectively and the pH reduced more than in the pure CO_2 scenario. They observed anhydrite corrosion by approximately 50 wt% and gypsum precipitation following the CO_2 plus NO_2 experiment (pressure and temperature of 77 bar and 49° C respectively). Parmentier et al. [10] performed a 30 day experiment on calcite minerals by injection of pure SO_2 and showed both calcite dissolution and anhydrite precipitation.

In our research project we experimentally investigated the impacts of various impurities on subsurface storage of CO_2 by using Permian Rotliegend reservoir and Zechstein caprock core samples. In this article we focus on H_2S and SO_2 as possible impurities, selected based on the results of capturing technology development. The impact of 100 ppm SO_2, 100 ppm H_2S and 5000 ppm H_2S co-injection with CO_2 was assessed experimentally (30 days duration) on Permian Rotliegend reservoir and Zechstein caprock core samples under subsurface conditions (300 bar and 100 °C) in depleted gas fields in northeast Netherlands. We compared the results of impure CO_2 injection with pure CO_2 injection. By selecting actual reservoir and caprock core samples rather than using single minerals we were in a position to measure permeability of the samples pre- and post-injection. In addition, Scanning Electron Microscopy (SEM) and X- Ray Diffraction (XRD) helped us to determine the mineralogy of the samples.

We complemented our experimental results with a modelling study, using the reactive surface area of minerals which were measured using SEM. The resulting ranges of reactive surface area for each mineral were implemented in TOUGHREACT [11] modelling software.

1. Experimental setup

The core samples were selected from Permian Rotliegend reservoir and Permian Zechstein anhydrite and carbonate components of caprock from wells in northeast Netherlands. The average mineralogy of the samples used for the pure CO_2 case is presented in Table 1. Depth range of the selected samples is between 2.9 and 3.0 km and porosity varies between 1% (caprock) and 27% (reservoir) while permeability ranges between 0.006 mD (caprock) and 6000 mD (reservoir).

Table 1. Average mineralogy (wt%) of Permian Rotliegend reservoir and Zechstein carbonate and anhydrite caprock

Mineral	Reservoir	Caprock	
		Anhydrite layer	Carbonate layer
Quartz	87		2.5
Kaolinite	5		
K-feldspar	2.5		
Dolomite	2	12.5	21.5
Albite	1.5		
Anhydrite	<1	87.5	8.5
Illite	<1		
Halite	0		3.5
Calcite	0		64

From core plugs, disk-shaped reservoir and caprock samples were cut with a 25-mm diameter. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used for the mineralogical analysis. These techniques were also utilized after the experiments to detect changes in mineralogy. SEM was carried out on a Philips XL-30 environmental SEM (ESEM) with Field Emission Gun (FEG). It is equipped with energy dispersive spectroscopy (EDS). Secondary Electron (SE) and Backscattered Electron (BSE) images were taken from the same spot on the core samples before and after the experiments. The X-ray diffraction analysis on the rock samples was performed with a Bruker D8 advance (40 Kv, 40 mA). Diffractometers recorded between 5° and 100 ° 2-Theta with $Cu\alpha_1$=1.54060 Å, $Cu\alpha_2$=1.54439 Å. The detector step size was set to 0.02 degree with 5 s/step. We used the GSAS (General Structure Analysis System) software to quantify different phases in the samples [12]. In addition, the permeability of the samples was measured pre- and post-experiment to determine possible changes. A standard core laboratory permeameter was utilized, with compressed dry air as a medium to flow through the samples at a rate regulated by a calibrated orifice. The permeability measurement error for reservoir and caprock samples is between 5 and 20% (lower error for higher permeability samples).

A batch experimental setup with reaction cells has been deployed to create the experimental conditions of 300 bars and 100° C, similar to the in situ reservoir condition. The reaction cells are made up of a metal alloy (38-46% Ni, 0-0.025% C, 1.5-3% Cu, balance Fe, 0-1% Mn, 19.5-23.5% Cr, 0-0.5% Si, 2.5-3.5% Mo and 0.6-1.2% Ti). These cells are able to tolerate a maximum pressure and temperature of 350 bars and 150 °C respectively with a capacity of 100 cm^3 (Fig. 1)

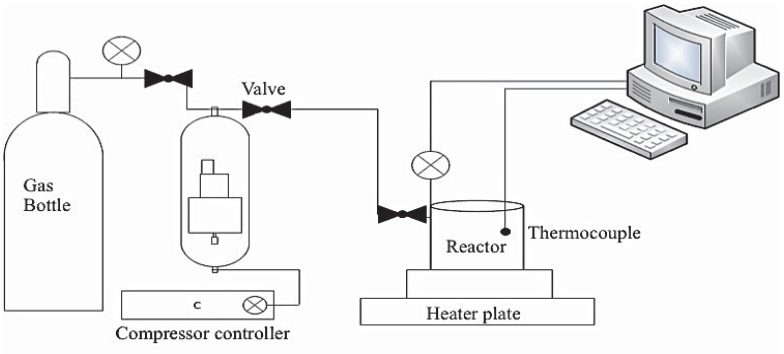

Fig. 1. Experimental setup [2,13]

The cylindrical reservoir and caprock core samples were brought in contact with brine with a composition obtained from gas well test data (85 g/L Na^+, 22g/L Ca^{2+}, 2.3 g/L Mg^{2+}, 173 g/L Cl^-, 1.5 g/L K^+, 0.05 gr/L S and pH of 6.8). In total 4 sets of experiments have been carried out which are:

- Pure CO_2 (30 days)
- CO_2+5000 ppm H_2S (30 days)
- CO_2+100 ppm H_2S (30 days)
- CO_2+100 ppm SO_2 (30 days)

In addition, one test was performed with pure CO_2 for the duration of 143 days in order to monitor the possibility of dawsonite precipitation. Two tests have been carried out with injection of CO_2 + 100 ppm H_2S for the period of 17 and 80 days to monitor permeability changes over time.

2. Results

2.1. Mineralogical variation

Following injection of CO_2 and impurities and their dissolution in the brine, the pH of brine reduces (Reaction 1-3).

$$CO_{2\ (aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (1)$$

$$4SO_2 + 4H_2O \leftrightarrow 3H_2SO_4 + H_2S \quad (2)$$

$$H_2S_{(aq)} \leftrightarrow 2H^+ + HS^- \quad (3)$$

Dissolution of CO_2 and SO_2 in brine lead to the formation of carbonic acid and sulfuric acid respectively (reaction 1,2). Also, dissolution of H_2S in brine forms H^+, which reduces the pH of the brine (reaction 3).

Increased brine acidity leads to the dissolution of feldspars, kaolinite and carbonate minerals (Fig. 2 and Fig. 3). Precipitation of kaolinite was observed in all experiments.

In addition to the above, several reactions occurred unique to each type of experiment:

1- After the 143-day experiment with pure CO_2 dawsonite precipitation was observed. This was not seen in the 30-day experiments
2- Co-injection of H_2S and SO_2 provided an additional source of sulphur leading to anhydrite precipitation. In the pure CO_2 experiment anhydrite dissolved.
3- After H_2S co-injection pyrite and halite were formed.

4- In the case of SO_2 co-injection enhanced levels of dissolution of feldspar and carbonate minerals occurred due to the formation of strong sulfuric acid

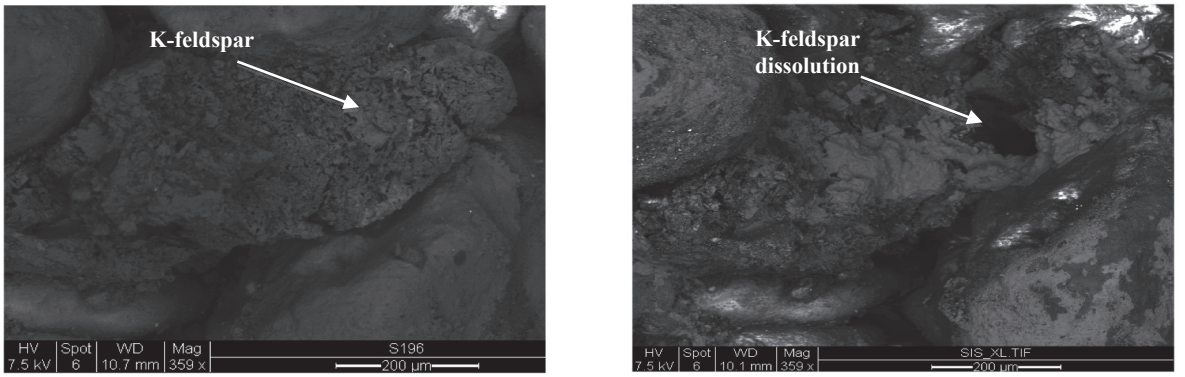

Fig. 2. (a) SEM image of a Rotliegend reservoir sample before the experiment (b) K-feldspar dissolution after pure CO_2 experiment [2]

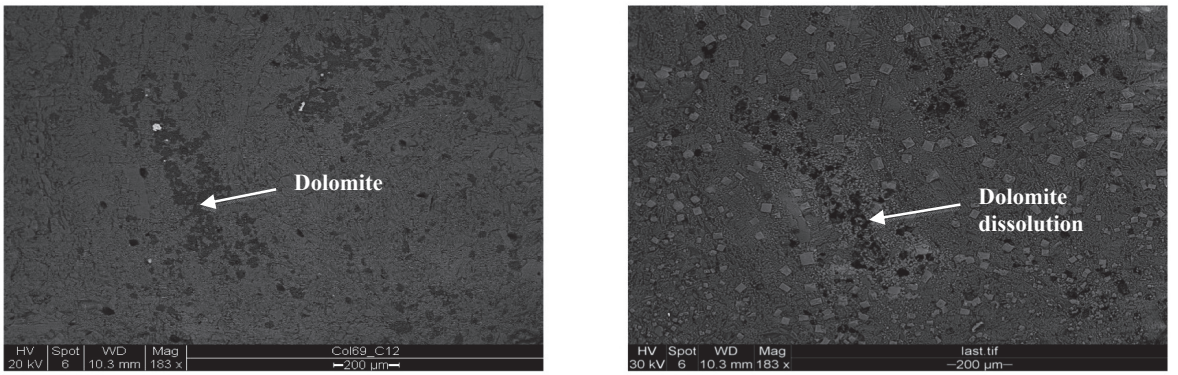

Fig. 3. (a) SEM image of a Zechstein caprock sample before the experiment. (b) Dolomite dissolution following SO_2 co-injection.

2.2. Permeability measurements

In order to evaluate the effects of mineral dissolution/ precipitation in the reservoir, we compared permeability of the samples before and after the experiments (Fig. 4).

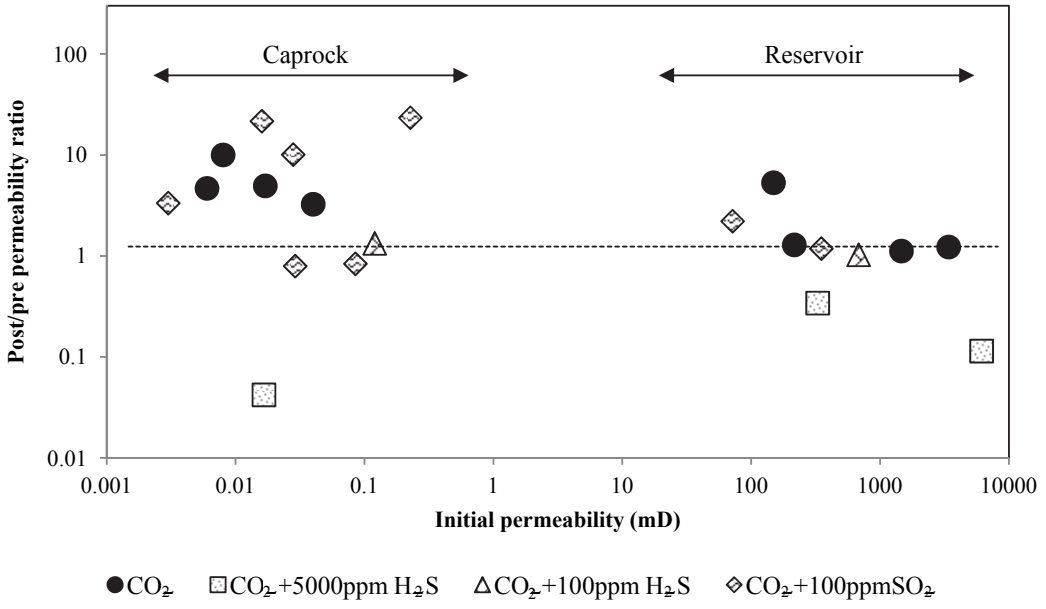

Fig. 4. Permeability comparison before and after CO_2, CO_2+ 5000 ppm H_2S, CO_2+ 100 ppm H_2S and CO_2+ 100 ppm SO_2 (30 days). The dashed line shows no change in the permeability (post to pre ratio is one). Above and below the dashed line reveals increase and decrease in the permeability respectively.

Following injection of CO_2 the permeability of all samples increased. For the reservoir samples the increase ranged between 10 and 30% (after 30 days), except for one sample where permeability increased by a factor of 5 (Fig. 4) [2]. The difference was that this sample had the lowest initial permeability and a higher content of cement material (carbonate and feldspars). In the cap-rock samples the permeability increased by a factor of 3-10.

After CO_2+ 5000 ppm H_2S injection, a significant decrease in permeability of both reservoir and caprock samples was observed (Fig. 4). Significant Halite and to a lesser degree pyrite and anhydrite precipitation are the reason of that.

After CO_2+100 ppm H_2S injection permeability remained almost unchanged (slight increase <3%) in the reservoir sample. In the cap-rock sample permeability increased by 30% which is far less than in the case of pure CO_2 injection. The reason is that secondary mineral precipitation (pyrite, anhydrite and halite) balances the dissolution of minerals [2]. This was confirmed by permeability measurements following CO_2+100 ppm H_2S injection for 17 and 80 days. After 17 days, permeability of the reservoir and caprock samples had dropped from 419 mD to 17.5 mD and 0.0058 mD to 0.0014 mD respectively. In this period the precipitation of halite did overcome dissolution of feldspar and carbonate minerals. However, over time the mineral dissolution process takes over and permeability increases again as concluded from the 30- and 80-day experiments (after the 80 day experiment, permeability of reservoir samples increase by 10-50%) [2]

Following co-injection of 100 ppm SO_2 along with CO_2 the permeability of the reservoir samples increased by a factor of 1.2 to 2.2, as expected and in line with the microscopic observations. In the caprock samples, permeability changed by a factor of 0.8 to 23. This wide range can be explained by the mineralogical composition of the samples. In the samples with higher initial carbonate mineral concentration compared to anhydrite content, the permeability increases due to the carbonate dissolution [14].

3. Discussion

Due to the limited time scale possible for laboratory experiments we need to rely on modeling programs in order to determine long term (>100 years) interaction between CO_2 and the reservoir mineralogy.

There are several critical parameters in the modeling software which need to be accurately addressed in order to obtain reliable and valid results. Some of these parameters are reactive surface area, dissolution/precipitation rate and activation energy of minerals. In this paper, we specifically focused on the on the effect of reactive surface area of the reservoir minerals.

3.1. Reactive surface area measurement

SEM was utilized to measure the reactive surface area of the minerals. More than 400 images were taken from the minerals present in the Rotliegend reservoir core samples, subsequently we used the crystallographic structure of minerals to transform the measurements into reactive surface areas. However, in reality the minerals did not always conform to these structures and hence a geometrical correction factor was applied. A summary of the minimum, maximum and mean surface area values of each mineral are given in Table 2 [13].

Table 2. Range of reactive surface area of the minerals in the Rotliegend reservoir (Reprinted after Bolourinejad et al. [13])

Mineral	Min surface area (m^2/m^3mineral)	Mean (P50) surface area (m^2/m^3mineral)	Max surface area (m^2/m^3mineral)
Quartz	7×10^3	1.24×10^4	3×10^4
Kaolinite	1.2×10^6	1.28×10^6	3.4×10^7
Dolomite	2.8×10^4	2.9×10^5	5×10^5
Albite	2.7×10^5	8.4×10^5	6.03×10^6
K-feldspar	2.7×10^6	6.27×10^6	1.8×10^7
Illite	7.2×10^6	1.57×10^7	4.8×10^7
Dawsonite	3.3×10^5	9.18×10^5	1.6×10^6

3.2. Implementation of reactive surface area in the model

Using the reactive surface area of the minerals TOUGHREACT [11] modeling software was used in order to model the behavior of CO_2 after injection in the reservoir. The storage reservoir is confined using a radial (R, Z) model with 5380 m radius and 109 m thickness. The model description can be found in detail in Bolourinejad et al. [13]. CO_2 is injected into the system at a rate of 4 kg/s for the period of 31 years, yielding a total of 3.91 Mt injected CO_2. Following cessation of injection, the reservoir is monitored for 250 years.

In total 129 simulations have been carried out to cover the range of measured reactive surface areas. In addition, one simulation has been carried out with the reactive surface area values taken from Xu et al. [6] which we took as a base case.

In order to assess the influence of mineral surface area on the dissolution/precipitation of that mineral, we can compare its final volume in the base case with the final volume using the experimentally determined surface area value (P50) (Fig. 5).

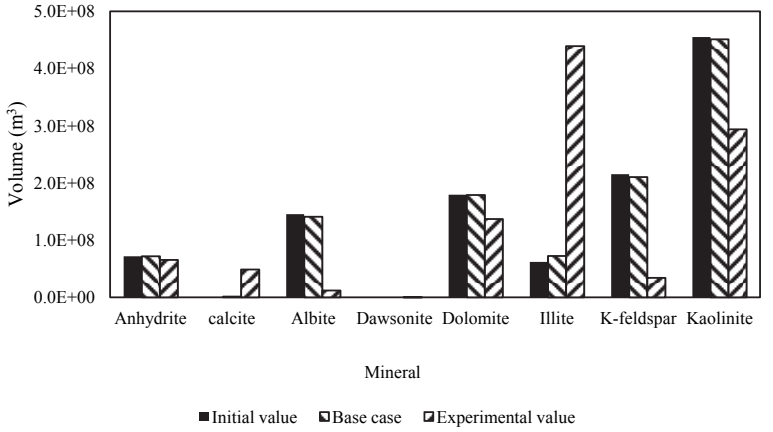

Fig. 5. Comparison of the mineral volume between utilizing base case surface area and experimental surface area (P50). Quartz is not shown in the graph due to its dominating volume in the reservoir rock. Quartsubmissioz volume increased by 0.7% using the experimental value compared to the base case value [13].

The modeled dissolution and precipitation of the minerals are stronger when utilizing the experimentally determined reactive surface areas. The reason is that these surface areas are at least one order of magnitude larger than those based on the literature values.

The distribution of total sequestered CO_2 as mineral ($SMCO_2$) from simulations is shown in Figure 6.

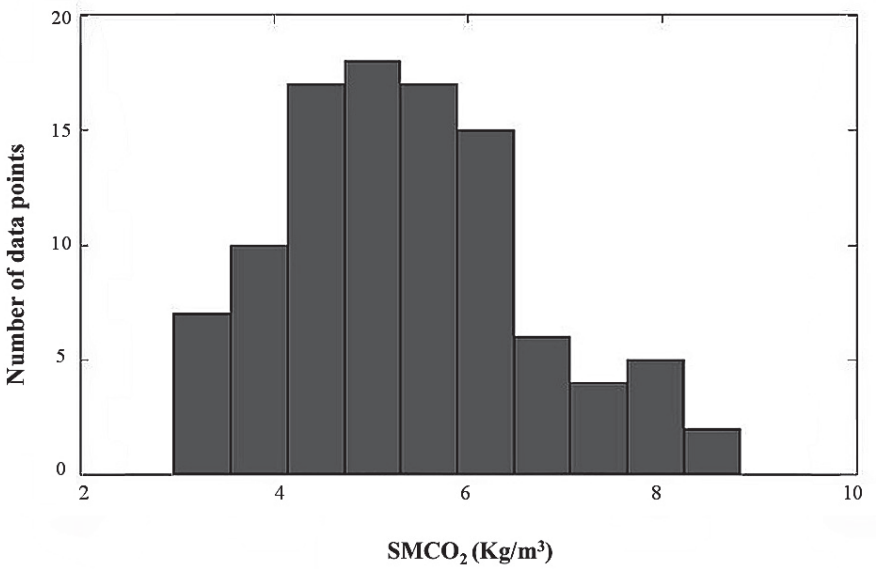

Fig. 6. (a) SMCO2 distribution within the experimental range of reactive surface area [13]

Using the range of experimentally determined reactive surface areas, $SMCO_2$ ranges between 3 to 9 kg/m^3 with a mean of 5.3 kg/m^3 (Fig. 5). This is significantly higher than the 0.8 kg/m^3 $SMCO_2$ for the base case. This is as expected since the experimental surface area values are significantly higher than the base case values.

The results presented in this paper provided new experimental information in the form of geochemical consequences of co-injection of SO_2 and H_2S with CO_2 in the subsurface. These results are field specific and dependent on many parameters such as mineralogy, brine composition, reactive surface area and grain size.

In addition, we showed that the reactive surface area of minerals is an important input parameter for modelling studies. There are also other parameters such as mineral dissolution/precipitation rate and activation energy which are necessary to be accurately measured in order to enable us to predict the magnitude of mineral trapping following injection of CO_2 in the subsurface.

4. Conclusion

In our study, we experimentally investigated the effects of injecting CO_2 in combination with impurities (H_2S and SO_2) on reservoir and caprock. The experimental set up was designed to be able to simulate the in-situ reservoir conditions (pressure 300 bar and temperature 100˚C) present in Rotliegend gas fields in northeast Netherlands.

Following the experiments, different mineralogical variations occurred:

- In all cases quartz, feldspar, kaolinite and carbonate dissolution has been observed.
- The magnitude of mineral dissolution was higher in the case of SO_2 co-injection. This is due to the formation of strong sulphuric acid.
- Precipitation of kaolinite occurred in all cases.
- Following H_2S and SO_2 co-injection anhydrite precipitated.
- After the CO_2 injection experiment, the permeability of reservoir and caprock samples increased 10-30% and by a factor of 3-10 respectively.
- Following CO_2+5000 ppm H_2S injection, significant reduction in the permeability of the samples was observed due to the precipitation of halite, pyrite and anhydrite. This can reduces the well injectivity.
- When the concentration of H_2S was reduced to 100 ppm, minimal changes occurred in the permeability of the samples, which is due to the balancing of mineral dissolution by precipitation of secondary minerals.
- In the case of SO_2 co-injection, permeability of the reservoir samples increased by a factor of 1.18-2.20. In the caprock samples, permeability changed by a factor of 0.8- 23. This wide range can be explained by caprock mineralogy. In the caprock samples with higher carbonate/ anhydrite ratio, permeability significantly increases due to the rapid dissolution of carbonate minerals.

In conclusion, from these experimental results we deduct that CO_2 leakage from caprock is dependent on the caprock mineralogy, brine composition and presence of impurities.

With respect to the modelling study, we focused on the reactive surface area of the minerals. SEM was utilized for surface area measurements. The produced range of reactive surface area were input in TOUGHREACT modelling software and we could obtain a range of values for changes in mineralogy and SMCO2 rather than being dependent on a single value.

- Using the range of experimentally determined reactive surface areas, $SMCO_2$ ranges between 3 to 9 kg/m^3 with a mean of 5.3 kg/m^3, which is higher than 0.8 kg/m^3 $SMCO_2$ obtained from the use of literature values of reactive surface area.

Prior to the start of large CO_2 projects, combined experimental and modelling research is necessary to be carried out on fields with specific properties such as mineralogy and brine composition. This sort of analysis can potentially minimise the risks associated with CO_2 storage such as leakage and loss of well injectivity. These safety aspects need to be combined with other parts of the CCS chain like transportation and pipelines in order to obtain a complete risk assessment analysis.

Acknowledgement

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